

The University of Chicago

THE CRYSTAL STRUCTURE OF POTASSIUM PERSULFATE

A DISSERTATION SUBMITTED TO THE
FACULTY OF THE DIVISION OF THE
PHYSICAL SCIENCES IN CANDIDACY FOR
THE DEGREE OF DOCTOR OF PHILOSOPHY

DEPARTMENT OF PHYSICS
1935

By
RICHARD CLIFTON KEEN

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The Crystal Structure of Potassium Persulfate $K_2S_2O_8$.

By

Richard C. Keen in Chicago.

(With one figure.)

Abstract.

The crystal structure of potassium persulfate was examined in order to compare the structure of the persulfate group in this crystal with that found in other compounds¹). It was found that the cell was triclinic and had the dimensions:

$$\begin{array}{lll} a = 5.10 \text{ \AA} & b = 6.83 \text{ \AA} & c = 5.40 \text{ \AA} \\ \alpha = 106^\circ 54' & \beta = 90^\circ 10' & \gamma = 102^\circ 35'. \end{array}$$

The space group was found to be $C_4'(P_1)$ and the structure may be given by the following parameters:

	<i>K</i>	<i>O</i> ₁	<i>O</i> ₂	<i>O</i> ₃	<i>O</i> ₄	<i>S</i>
<i>x</i>	$\pm 67^\circ$	$\pm 31^\circ$	$\pm 110^\circ$	$\pm 192^\circ$	$\pm 77^\circ$	$\pm 93^\circ$
<i>y</i>	$\pm 70^\circ$	$\pm 32^\circ$	$\pm 82^\circ$	$\pm 85^\circ$	$\pm 162^\circ$	$\pm 87^\circ$
<i>z</i>	$\pm 185^\circ$	$\pm 25^\circ$	$\pm 107^\circ$	$\pm 35^\circ$	$\pm 40^\circ$	$\pm 7^\circ$

In the lattice each potassium atom is surrounded by ten oxygen atoms at an average distance of 3.08 Å. Two sulfur atoms and eight oxygen atoms are grouped together in the S_2O_8 group. The distance between the two oxygen atoms forming the bond in the S_2O_8 group was found to be 1.40 Å. The distance between sulfur atoms in same persulfate group is 3.86 Å. The average sulfur to oxygen distance in a SO_4 tetrahedron was found to be 1.51 Å.

Introduction. The chief purpose of this investigation was to determine the size and shape of the persulfate radical such as it appears in potassium persulfate in order to see if there are any appreciable differences from the structure found for this group in the ammonium persulfate and caesium persulfate¹).

According to Groth²) the crystal is triclinic and has holohedral symmetry. The axial ratios and angles

$$\begin{array}{lll} a:b:c = 0.5759:1:0.5740 \\ \alpha = 98^\circ 33' & \beta = 94^\circ 2' & \gamma = 88^\circ 39'. \end{array}$$

1) Zachariasen and Mooney, Z. Kristallogr. (A) 88 (1934) 63—81.

2) von Groth, P., Chem. Kryst. 2, 724.

Gerstäcker, Möller and Reis¹) found one molecule per unit cell, so that the number of parameters, although large, is not prohibitive. They have also found the axial ratios

$$a:b:c = 0.7844:1:0.8416$$

and a unit cell having dimensions and angles

$$\begin{array}{lll} a = 5.11 \text{ \AA} & b = 6.51 \text{ \AA} & c = 5.48 \text{ \AA} \\ \alpha = 96^\circ 45' & \beta = 90^\circ 10' & \gamma = 95^\circ 15'. \end{array}$$

The crystals used in this investigation were prepared by dissolving some potassium persulfate in distilled water to form a concentrated solution at atmospheric temperature and allowing the solution to slowly evaporate. It was found, that if water above atmospheric temperature was used to prepare the solution the crystal invariably twinned as stated by Groth.

Cell Size and Space Group. Complete sets of oscillation photographs were taken about the a and c axes; oscillating from 0° to 15° ; 10° to 25° ; 20° to 35° and so on up to 180° . One photograph was taken about the b axis to check the periodicity in the b direction. Laue photographs were taken with the beam perpendicular to the a and c axes using a radiation having a minimum wave length of $0.27 \text{ \AA}$. The Laue photographs were indexed by means of gnomonic projections and the oscillation photographs were indexed according to the graphical method described by Bernal²).

The dimensions of the unit cell were found to be:

$$\begin{array}{lll} a = 5.10 \pm .03 \text{ \AA} & b = 6.83 \pm .04 \text{ \AA} & c = 5.40 \pm .03 \text{ \AA} \\ \alpha = 106^\circ 54' & \beta = 90^\circ 10' & \gamma = 102^\circ 35'. \end{array}$$

This gives the axial ratios of

$$a:b:c = 0.7466:1:0.7907.$$

These dimensions with a density of 2.477 grams per c. c. give one (1.04) molecules per unit cell. No simple relationship was found between the system of axes used here and those used by Groth or by Messrs. Gerstäcker, Möller and Reis.

1) Gerstäcker, A., H. Möller, A. Reis, *Z. Kristallogr.* **66** (1927) 355.

2) Bernal, J. D., *Proc. Roy. Soc. London (A)* (1926) 113, 117.

The positions in the space group are:

Centers of Symmetry		General Positions
(a) 0 0 0	(e) $\frac{1}{2}$ $\frac{1}{2}$ 0	(i) $\pm x y z$
(b) 0 0 $\frac{1}{2}$	(f) $\frac{1}{2}$ 0 $\frac{1}{2}$	
(c) 0 $\frac{1}{2}$ 0	(g) 0 $\frac{1}{2}$ $\frac{1}{2}$	
(d) $\frac{1}{2}$ 0 0	(h) $\frac{1}{2}$ $\frac{1}{2}$ $\frac{1}{2}$	

Since the SO_4 group has no center of symmetry it is at once apparent that all the oxygen and sulfur atoms must lie in general positions. The potassium atoms may lie in either general positions or in the centers of symmetry.

Determination of the Structure. From a knowledge of the oxygen to oxygen distance for oxygen atoms not in the same SO_4 group it is possible to eliminate considerable space surrounding each center of symmetry in which no oxygen and sulfur atoms can lie. From the value of the scattering power of the atoms appearing in the compound it will be observed that for large values of $\sin \theta/\lambda$ the scattering power of potassium and sulfur are approximately equal while that due to oxygen is reasonably small compared to either of these two but not negligible.

Table I. F -Curves¹).

$\sin \theta/\lambda$	0.1	0.2	0.3	0.4	0.5	0.6
<i>K</i>	16.5	13.4	10.7	8.9	7.8	6.8
<i>S</i>	11.8	10.0	8.8	7.8	6.8	6.0
<i>O</i>	7.5	5.4	3.8	2.7	2.1	1.8

Due to the large number of oxygen atoms in the compound the probability that a large number of oxygen atoms will scatter in phase for any given plane is comparatively small. Therefore it should be possible to account for the majority of the observed intensities using only potassium and sulfur. This will not be true for all planes. Certainly any plane whose value of $\sin \theta/\lambda$ is greater than about 0.4 would not show any appreciable intensity if the potassium and sulfur atoms were not partially cooperating. By using a large number of these planes having indices $hk0$, $h0l$ and $0kl$ the approximate positions of the potassium and sulfur atoms were located. Use was made of the potassium to sulfur distances to show these results

1) James and Brindley, Z. Kristallogr. 78 (1931) 470.

to be reasonable. Having found the approximate position of the potassium and sulfur atoms it was assumed that four oxygens formed a tetrahedral configuration around the sulfur and that the sulfur to oxygen distance was approximately 1.50 Å. It was then possible to determine the position of the oxygen atoms using planes whose value of $\sin \theta/\lambda$ is small and the scattering power of oxygen is comparable to potassium and sulfur. By this method the following intensities were computed for planes having indices $hk0$, $h0l$ and $0kl$ and also for planes having general indices hkl .

Table II.

Calculated and Observed Intensities of $hk0$ reflections.

$hk0$	$\sin \theta/\lambda$	F	I	$hk0$	$\sin \theta/\lambda$	F	I
100	.10	8.0	W	$\bar{2}40$	.33	3.3	VW
110	.12	5.8	M	310	.35	12.6	VVW
020	.16	53.4	VS	140	.37	16.8	W-
$\bar{1}20$	.17	4.7	W	$\bar{1}50$	.38	25.4	MW
120	.21	27.0	S-	$\bar{3}40$	.38	6.7	W
200	.21	34.9	S	$\bar{2}50$	.40	15.3	M
$\bar{2}20$	.23	17.1	MS	050	.40	21.0	M
$\bar{1}30$	.23	7.4	W	320	.40	0.6	Nil
030	.24	34.7	M-	400	.41	20.0	W
210	.24	18.4	S	240	.42	33.2	S-
$\bar{1}40$	.26	5.3	Nil	150	.43	24.3	W-
$\bar{2}30$	.27	41.6	MS	$\bar{2}60$	.45	8.8	Nil
300	.28	21.7	Nil	330	.45	4.4	Nil
130	.30	4.3	Nil	350	.45	35.0	MS
220	.30	28.9	W-	060	.48	17.4	W
$\bar{3}20$	.31	20.0	W-	340	.50	4.3	Nil
040	.32	28.1	M				

Table III.

Calculated and Observed Intensities of $0kl$ Reflections.

$0kl$	$\sin \theta/\lambda$	F	I	$0kl$	$\sin \theta/\lambda$	F	I
011	.10	14.1	S	031	.23	27.5	MS
011	.14	3.2	M-	032	.27	17.5	MW
021	.17	0.1	VW	022	.28	31.2	S
012	.20	38.9	S	003	.28	1.3	W
021	.21	9.0	M-	013	.28	6.7	VW
002	.21	47.1	VS	013	.33	6.0	Nil
022	.21	22.0	MS	023	.33	3.9	Nil
012	.23	9.3	VW				

Table IV.

Calculated and Observed Intensities of $h0l$ Reflections.

$h0l$	$\sin \theta/\lambda$	F	I	$h0l$	$\sin \theta/\lambda$	F	I
101	.44	8.7	S—	203	.36	15.1	Nil
$\bar{1}01$	.45	13.0	S	$\bar{3}02$	.38	17.7	W—
102	.22	5.0	Nil	302	.39	21.5	W
$\bar{2}01$	.22	26.1	MS	$\bar{1}04$	.40	6.3	VW
$\bar{1}02$	.23	22.1	W	105	.42	4.2	VVW
201	.24	11.4	W—	401	.42	23.8	W—
$\bar{2}02$	.27	15.5	MS	$\bar{2}04$	.44	22.3	M
202	.30	28.1	MS	303	.45	22.7	MW
$\bar{1}03$	.32	1.4	M—	$\bar{3}03$	.45	23.7	M+
103	.32	19.5	MS	204	.46	28.5	MW
$\bar{3}01$	.33	17.4	MW	205	.50	12.7	Nil
301	.35	17.5	MS	$\bar{2}05$	.50	10.0	Nil
$\bar{2}03$	.36	7.9	Nil	304	.51	14.8	Nil

Table V. Final Parameter Values.

In angular measure				In fractions of cell dimensions		
	$2\pi x$	$2\pi y$	$2\pi z$	x	y	z
K	$\pm 67^\circ$	$\pm 70^\circ$	$\pm 185^\circ$	0.186	0.194	0.514
O_1	± 31	± 32	± 25	0.086	0.089	0.069
O_2	± 110	± 82	± 107	0.306	0.228	0.298
O_3	± 192	± 85	± 35	0.534	0.236	0.097
O_4	± 77	± 162	± 40	0.214	0.450	0.111
S	± 93	± 87	± 7	0.258	0.241	0.019

Table VI. Interatomic Distances.

$K - O_1$	2.90 Å	$K - O_4$	2.70 Å	$O_1 - O_1$	1.40 Å
	3.30		3.45	O_2	2.40
	3.40			O_3	2.43
O_2	2.75	$S - O_1$	1.52	O_4	2.51
	2.80	O_2	1.51	$O_2 - O_3$	2.42
	2.80	O_3	1.53	O_4	2.40
O_3	2.75	O_4	1.48	$O_3 - O_4$	2.42
	3.50	$S - S$	3.86		

Average Values: $K - O$ 3.08 Å $S - O$ 1.51 Å $O - O$ 2.43 Å

Discussion of the Structure.

The above observed and computed intensities are not in perfect agreement. The discrepancies which appear are perhaps due to slight errors in the parameters. Since there is such a large number of independent parameters it may require considerable shifting to eliminate all the discrepancies since there is no way of predicting which ones are

incorrect. Since the proposed structure accounts in a general way for the optical properties of the crystal, for its cleavage plane and the computed interatomic distances are all close to the accepted values, the structure seems satisfactory.

Figure 1 shows a diagram of the projection of the structure on a plane normal to the c axis.

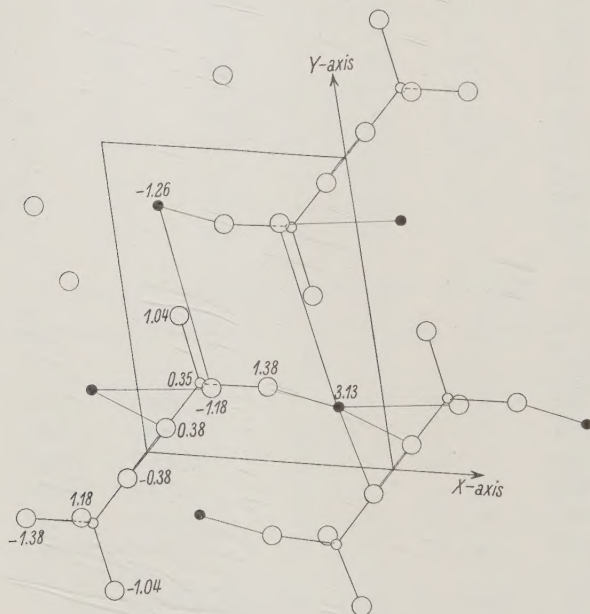


Fig. 1. The atomic arrangement in potassium persulfate projected on to a plane normal to the c -axis. The small filled circles represent the potassium atoms, the large open circles represent the oxygen atoms, the small open circles represent the sulfur atoms. The numerals represent the distances of the atoms above or below the plane.

Each potassium atom is surrounded by ten oxygen atoms at an average distance of $3.08 \text{ \AA}$. Sulfur is surrounded by four oxygen atoms at an average distance of $1.51 \text{ \AA}$, the four oxygens forming the four corners of a nearly regular tetrahedron. This is in good agreement for the dimensions of the SO_4 group as it appears in other compounds. The SO_4 groups are found to be linked into pairs by a valence bond similar to that found in the ammonium persulfate group. The size and the shape of the persulfate radical in this compound was found to have no appreciable differences from that found in the ammonium persulfate.

The shortest distance between oxygen atoms not in the same persulfate group was found to be 2.90 Å. This is not in such good agreement with the predicted value of 3.45 Å from ionic radii. The distance between two oxygen atoms linked together by a valence bond was found to be 1.40 Å. This value cannot be very accurately fixed but is in good agreement with the value 1.45 Å found in ammonium persulfate. The angle between two bonds to a similar oxygen atom (arbitrarily called O_1) in the persulfate group was found to be 115° .

The optical properties of this proposed structure is in agreement with the optical properties of the crystal as given by Groth. Consideration of the structure shows that the oxygen atoms which surround the potassium are arranged more or less evenly over the surface of a sphere and consequently will polarize the potassium atom approximately the same for all directions of the electric vector in the incident light. The SO_4 part of the persulfate group has tetrahedral symmetry and consequently does not contribute anything to the anisotropic properties of the crystal. The manner in which the two O_1 atoms of the persulfate group are linked to each other represents a very highly anisotropic configuration and as such is responsible for nearly all the birefringence observed in the crystal. Since there is only one molecule per unit cell in the crystal all these valence bonds must be parallel. If the electric vector of the incident light is parallel to the direction of the bond the induced moment in one of the O_1 atoms will create a comparatively strong field on the other oxygen atom having the same direction as the external field. If the electric vector is normal to the direction of the bond between the two O_1 atoms the induced moment in one of the oxygen atoms will set up in the other a field which opposes the external field. Therefore the crystal should be optically positive with strong birefringence. The acute bisectrix should be nearly parallel to the direction of the valence bond between the two oxygen atoms and the angle, $2V$, should be small. All these optical properties are given by Groth.

The proposed structure also accounts for the cleavage property mentioned by Groth. In the b direction there are only two potassium to oxygen bonds which would account for very pronounced cleavage.

In conclusion I wish to express my sincere appreciation to Dr. W. H. Zachariasen for suggesting the problem and for his many helpful suggestions during the course of solution.

Ryerson Physical Laboratory, University of Chicago, Feb. 1935.

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